

Correlation between Positron Annihilation and Gas Diffusion Properties of Various Rubbery Polymers

Ken-ichi OKAMOTO,[†] Kazuhiro TANAKA, Mikio KATSUBE,
Hidetoshi KITA, Osamu SUEOKA,* and Yasuo ITO**

*Department of Advanced Materials Science and Engineering, Faculty of Engineering,
Yamaguchi University, Ube, Yamaguchi 755, Japan*

** Department of Applied Science, Faculty of Engineering, Yamaguchi University,
Yamaguchi 755, Japan*

*** Research Center for Nuclear Science and Technology, The University of Tokyo,
Tokaimura, Ibaraki 319-11, Japan*

(Received August 21, 1992)

ABSTRACT: Diffusion coefficients D for CO_2 and CH_4 , their activation energies, E_D , and lifetime and intensity of *ortho*-positronium (*o*-Ps), τ_3 and I_3 respectively, were measured for nine polymers at temperatures T from glass transition temperature T_g up to $T_g + 70$ K. For semicrystalline polymers, D and I_3 are corrected to give those in 100% amorphous samples, D_a and $I_{3,a}$, respectively. Average size of free volume holes probed by *o*-Ps, $v_{h,Ps}$, is evaluated from τ_3 using an empirical equation. According to the free volume model of diffusion, correlations between $\log(D_a/T)$ and fractional free volume f and between E_D/RT and $Tf^{-2}(df/dT)$ are tested, using WLF fractional free volume f_{WLF} , $v_{h,Ps}I_3$, and $v_{h,Ps}$ for f . The correlations are better for $v_{h,Ps}$ than for $v_{h,Ps}I_3$. There is no correlation for f_{WLF} . The volume fraction of free volume holes larger than the effective size of the penetrants, $V_{F,dif}$, are evaluated by a proposed model from $v_{h,Ps}$ and volume fraction of 'free space,' V_F , estimated by the method of van Kreveran and Bondi. The correlations are better for $V_{F,dif}$ than for V_F and also for $v_{h,Ps}$. The apparent good correlations for $v_{h,Ps}$ are ascribed to the correlation of it with $V_{F,dif}$.

KEY WORDS Diffusion Coefficient / Rubbery Polymer / Free Volume / Positron Annihilation / *ortho*-Positronium / Carbon Dioxide / Free Volume Distribution /

Diffusion of penetrant molecules in polymers is a subject of great importance from the standpoint of membrane separation. Diffusion of penetrants in rubbery polymers is often interpreted by free volume theory.¹⁻³ According to Fujita's formulation,¹ the diffusion coefficient, D_0 , at zero penetrant concentration is given by

$$D_0 = A_d RT \exp(-B_d/f) \quad (1)$$

where A_d and B_d are the parameters dependent on penetrant molecular size and shape, R is the gas constant, T temperature, and f

fractional free volume. The fractional free volume is generally expressed by

$$f = f_g + (\alpha_1 - \alpha_g)(T - T_g) \quad (2)$$

where f_g is the fractional free volume at the glass-transition temperature T_g , and α_1 and α_g are the thermal expansion coefficients above and below T_g , respectively. Williams-Landel-Ferry (WLF) fractional free volume derived from viscosity theories,^{4,5} f_{WLF} , in which f_g is taken as 0.025, is often used. Free volume in a rubbery polymer is generally considered to be composed of a spectrum of cavities

[†] To whom correspondence should be addressed.

produced spontaneously by density fluctuations, namely, free volume elements (or holes). A portion of the free volume distribution involved in diffusion, which depends on the size of penetrant molecules, is not necessarily identical with that in viscosity.³

Positron annihilation (PA) in polymers has recently attracted much interest because PA is expected to bring forth information about their microstructure.⁶ PA lifetime spectra of polymers have a long-lived component which is attributed to *ortho*-positronium (*o*-Ps) formed and annihilated in amorphous regions. The lifetime of the long-lived component, τ_3 , is considered to be a good measure of the size of the micro-vacancies where *o*-Ps is trapped. The intensity of the long-lived component, I_3 , is sometimes considered to be a measure of the number of such microvacancies. However, it is not mature to correlate I_3 with the number of such vacancies.

The micro-vacancies seen by *o*-Ps in rubbery polymers are presumed to be free volume holes large enough to accommodate *o*-Ps. Thus, free volume holes with the effective diameter larger than *ca.* 0.4 nm are expected to be probed by *o*-Ps. This portion of the free volume distribution is close to that involved in the diffusion of gases such as CO₂ and CH₄. Therefore, it is interesting to compare the PA properties of rubbery polymers with gas transport properties.

Volkov *et al.* compared gas sorption and diffusion with PA properties for some rubbery polymers at room temperature.^{7,8} They claimed the following; (1) $\tau_3 I_3$ is smaller for polymers having higher T_g and approaches zero when T_g is the experimental temperature (room temperature), suggesting that the free volume measured by the PA method is related mainly to the segmental mobility; (2) Logarithms of D and of the solubility coefficient S are closely correlated with $(\tau_3 I_3)^{-1}$ and τ_3^{-1} , respectively. However, most of the rubbery polymers investigated by Volkov *et al.* have T_g values lower than 200 K, and the

PA data for these polymers measured at room temperature are considered to originate not from the free volume holes in equilibrium controlling diffusion process but from Ps bubbles.

In the previous paper,⁹ we investigated PA properties of several polymers over wide temperature ranges above and below T_g , and confirmed that the PA data measured at temperatures not much above T_g reflect the properties of free volume holes in equilibrium state rather than those of Ps bubbles. We also discussed the fraction of free volume holes probed by *o*-Ps and proposed a method to evaluate it from the PA data.

In this study, gas transport properties and PA properties have been examined for various rubbery polymers at temperatures not much above T_g to investigate how clearly diffusion coefficients for gases are correlated with the PA properties such as the volume fraction of free volume holes probed by *o*-Ps.

EXPERIMENTAL

The samples used in this study are as follows; low-density polyethylene (PE), 1,2-polybutadiene (1,2-PB), poly(4-methylpentene (P4MP-C), poly(ethylene terephthalate) (PET), poly(vinyl acetate) (PVAC), poly(styrene) (PS), poly(methyl acrylate) (PMA), poly(buthyl methacrylate) (PBMA), and polyimide (6FDA-DAH PI) prepared from 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 1,6-diaminohexane (DAH). The additive-free films of PE, P4MP-C, and PET were supplied from Ube Industries Ltd., Mitsui Petrochemical Industries Ltd., and Mitsubishi Plastics Ltd., respectively. P4MP-C is a copolymer of 4-methylpentene-1 with a small content of α -olefine (C₁₈ component). Amorphous PET films (Diafoil) were heat-treated at 408 K for 12 h *in vacuo*. 1,2-PB supplied from Japan Synthetic Rubber Ltd. was purified by repeated reprecipitations (toluene/methanol). Films of 1,2-PB, PVAC,

PS, PMA, and PBMA were cast from their benzene solutions onto glass plates, and dried at 323 K (300 K for PMA) for 20 h *in vacuo*.⁹ 6FDA-DAH PI was prepared by the method described elsewhere,¹⁰ and its films were cast from the dichloromethane solutions and dried at 373 K for 20 h *in vacuo*. Characterization of the films were carried out by the methods described in the previous paper.⁹

Gas sorption and transport experiments were carried out by the methods described elsewhere.^{10,11} The vacuum time-lag method was used to measure permeability coefficient P and diffusion time-lag θ . A dual-volume type sorption cell was used to measure solubility coefficient S . The P and S were measured for CO_2 and CH_4 at 1 atm and at temperatures from T_g up to $T_g + 70$ K. Diffusion coefficient D was calculated from either $D = P/S$ or $D = l^2/(6\theta)$ where l is film thickness.

The PA lifetime measurements were carried out at the Inter-University Laboratory for the Common Use of JAERI facilities.¹² The details are described in the previous papers.^{9,13} Each spectrum, having more than one million total count, was analyzed into three lifetime components using the computer program PATFIT.¹⁴

RESULTS AND DISCUSSION

Characterization results of the polymer films are listed in Table I. The amorphous fraction ϕ_a were determined from the X-ray diffraction patterns and the densities ρ . The details have been described in the previous paper.⁹ Fraction of 'free space' V_F refers to the ratio of the so-called 'expansion volume'¹⁵ to the observed volume and was calculated by

$$V_F = (V_T - V_0)/V_T \quad (3)$$

where V_T is the molar volume at temperature T and V_0 is the volume occupied by the molecules at 0 K per mole of repeat unit of the polymer. V_T was calculated from the observed value at 298 K using α_g and α_l . V_0 was estimated to be 1.3 times¹⁵ the van der Waals volume calculated by the group contribution method of Bondi.¹⁶

The average volume of the free volume holes probed by *o*-Ps, $v_{h,Ps} [(4/3)\pi R^3]$, was calculated by the following equation between τ_3 and the average radius R of microvacancies.^{17,18}

$$\tau_3 = (1/2)[1 - (R/R_0) + (1/2\pi)\sin(2\Delta R/R_0)]^{-1} \quad (\text{ns}) \quad (4)$$

$$R_0 = R + \Delta R, \quad \Delta R = 0.166 \text{ nm}$$

Table I. Characterization results of polymer films^a

Polymers	T_g	ρ	ϕ_a	α_g	α_l	V_F
	K	g cm^{-3}	—	10^{-4} K^{-1}		—
1,2-PB	249	0.900	0.85	1.93	6.5	0.200
PE	251	0.910	0.63	2.8	7.5	0.192
PMA	280	1.209	1.0	2.7	5.6	0.159
P4MP-C	295	0.835	0.65	3.71	7.38	0.209
PBMA	307	1.051	1.0	4.02	6.45	0.164
PVAC	304	1.190	1.0	1.71	5.06	0.176
PET	361	1.376	0.67	2.47	6.20	0.149
PS	377	1.045	1.0	2.11	5.57	0.180
6FDA-DAH	397	1.424	1.0	2	5 ^b	0.137

^a ρ and V_F are at 298 K.

^b The α_l value of 6FDA-DAH PI was assumed to be $5 \times 10^{-4} \text{ K}^{-1}$ because it could not be measured by means of the thermomechanical analysis.

Table II. Diffusion coefficients D and activation energies E_D for CO_2 and CH_4 in rubbery polymers^a

Polymer	l μm	T K	CO_2		CH_4	
			D	E_D	D	E_D
1,2-PB	166	293	49	31	15.3	38
		308	91		33	
PE	47	303	58	45	35	51
		313	107		86	
		323	180		119	
PMA*	40	283	0.47	62	—	—
		298	2.2		1.64	
		303	3.1		—	
		308	3.7		3.0	
P4MP-C	54	303	—		43*	(28)
		308	104	30	78	
		323	180		109	
PBMA	77	308	31	34	25	38
		323	57		49	
PVAC	38	313	1.2	70	0.32	92
		323	2.7		0.96	
PET*	54	363	2.2	68	0.84	75
		378	5.3		2.4	
		393	12		5.6	
PS*	220	378	93	38	39	52
		388	117		53	
		403	190		108	
6FDA-DAH	64	403	8.1	—	2.6	—

^a D is in $10^{-8} \text{ cm}^2 \text{ s}^{-1}$, and E_D is in kJ mol^{-1} . The D data for the polymers asterisked were determined from the time lag. The l values are for typical films.

The long-lived component is assigned to o -Ps annihilating in the amorphous region. It has been found for semicrystalline polymers that I_3 linearly depends on ϕ_a but τ_3 does not.¹⁹ I_3 values for the semicrystalline polymers were, therefore, corrected to give those in 100% amorphous samples, $I_{3,a}$, as

$$I_{3,a} = I_3 / \phi_a \quad (5)$$

The data of D are summarized in Table II. The D for CO_2 and CH_4 in the rubbery polymers used here is practically independent of feed pressure below 5 atm. Therefore, the D values measured at 1 atm can be regarded as the D_0 values. The D values for the semicrystalline polymers were corrected to give those in 100% amorphous samples, D_a , as

$$D = D_a / \tau\beta \quad (6)$$

where τ is the tortosity factor, and β is the chain immobilization factor. The τ was approximated as $\tau = \phi_a^{-1}$.²⁰ The β was approximated as 1.0–1.1 for CO_2 and 1.0–1.4 for CH_4 , depending on ϕ_a .²¹

Correlation of D_a with WLF Fractional Free Volume

A linear correlation between $\log(D_a/T)$ and f_{WLF}^{-1} is predicted from eq 1, provided that the parameters A_d and B_d for a given penetrant does not much vary from polymer to polymer. Figure 1 shows plots of $\log(D_a/T)$ versus f_{WLF}^{-1} for CO_2 in the rubbery polymers. From the viewpoint of WLF free volume, the glass transition is described as an isofree volume state. As can be seen in Figure 1, the values of D_a/T near T_g vary by 150 times and no linear relation between $\log(D_a/T)$ and

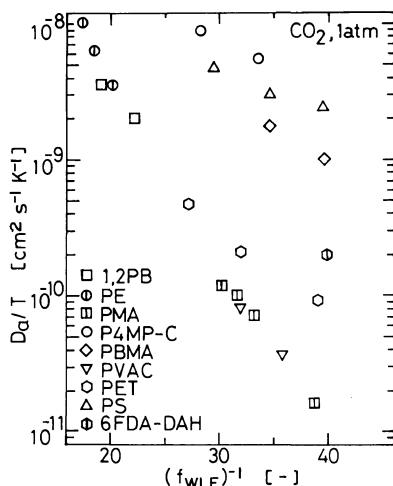


Figure 1. Plots of $\log(D_a/T)$ versus f_{WLF}^{-1} for rubbery polymers.

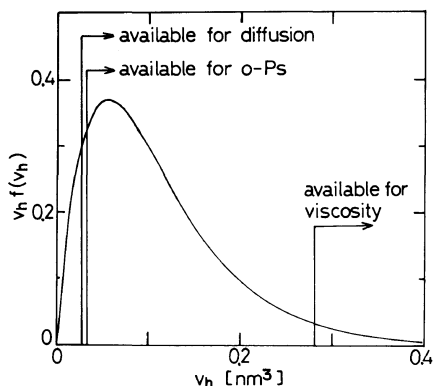


Figure 2. Typical example of the distribution function of fractional free volume.

f_{WLF}^{-1} is observed. The situation is the same for CH_4 . The large variation in D/T_g for Ar was also reported for other polymers.^{22,23} This result might be explained by considering the difference in the segmental mobility. However, it would be important to take the size distribution of the fluctuating free volume holes into account.

The distribution function of the size of free volume holes, $f(v_h)$, for rubbery polymers is described by

$$f(v_h) = (1/\langle v_h \rangle) \exp(-v_h/\langle v_h \rangle) \quad (7)$$

where $\langle v_h \rangle$ is a mean size of free volume holes.²⁴ Figure 2 illustrates the distribution function of fractional free volume, $v_h f(v_h)$. Only the free volume holes large enough for a chain segment of a given polymer to be accommodated can contribute to the viscosity of the polymer and consequently WLF fractional free volume involves only this portion of free volume distribution. On the other hand, the free volume holes large enough for a penetrant molecule to pass through can contribute to the diffusion of the penetrant. The effective diameters for diffusion of CO_2 and CH_4 are 0.35 and 0.38 nm, respectively.^{25,26} Therefore, free volume holes larger than v_h of about 0.029 nm^3 are presumed to contribute to the diffusion of these penetrants. The volume fraction of such free volume holes, $V_{F,dif}$ is much larger than f_{WLF} and rather close to the volume fraction of free volume holes probed by *o*-Ps, $V_{F,Ps}$. This should be the reason that there is no correlation between $\log(D_a/T)$ and f_{WLF}^{-1} .

Correlation of D with $v_{h,Ps}I_{3,a}$ and $v_{h,Ps}$

From the above discussion it is suggested that either $V_{F,dif}$ or $V_{F,Ps}$ should be used for f in eq 1 instead of f_{WLF} . However, $V_{F,dif}$ can not be evaluated directly without any assumption. $V_{F,Ps}$ is given by the product of $v_{h,Ps}$ and the concentration of free volume holes probed by *o*-Ps, $C_{h,Ps}$. Volkov *et al.* presumed that $\tau_3 I_3$ is proportional to the fractional free volume and found a clear correlation between $\log D$ and $(\tau_3 I_3)^{-1}$ for five rubbery polymers at room temperature.^{7,8} Therefore, presuming that $v_{h,Ps} I_{3,a}$ is a direct measure of f , we first examine how clearly $\log(D_a/T)$ is correlated to $v_{h,Ps} I_{3,a}$ for the rubbery polymers at temperatures not much above T_g . Figure 3 shows plots of $\log(D_a/T)$ for CO_2 versus $(v_{h,Ps} I_{3,a})^{-1}$. There is a correlation between them except for 6FDA-DAH PI. The data point ($D/T = 2 \times 10^{-10}$ and $(v_{h,Ps} I_{3,a})^{-1} = 137$) for 6FDA-DAH PI is very apart from the correlation line. From the slope of the correlation

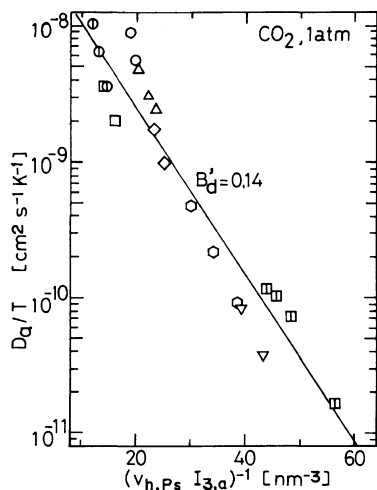


Figure 3. Plots of $\log(D_a/T)$ versus $(v_{h,Ps}I_{3,a})^{-1}$ for rubbery polymers. The symbols are as in Figure 1.

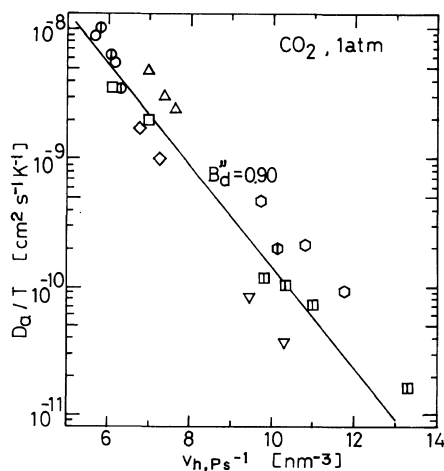


Figure 5. Plots of $\log(D_a/T)$ versus $v_{h,Ps}^{-1}$ for rubbery polymers. The symbols are as in Figure 1.

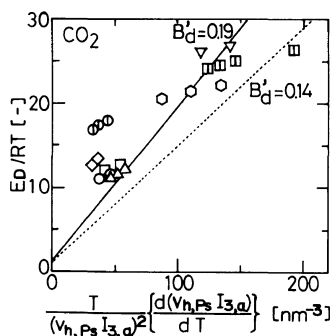


Figure 4. Plots of E_D/RT versus $T(v_{h,Ps}I_{3,a})^{-2}d(v_{h,Ps}I_{3,a})/dT$ for rubbery polymers. The symbols are as in Figure 1.

line, B_d' ($=B_d v_{h,Ps} I_{3,a} / f$) is evaluated to be 0.14 nm^3 . The correlation is much clearer for CO_2 than for CH_4 .

The temperature dependence of the diffusion coefficients is considered to be of Arrhenius type with the apparent activation energies E_D listed in Table II. From the viewpoint of the free volume model of diffusion, E_D is described by

$$E_D/RT = 1 + B_d T f^{-2} (df/dT) \quad (8)$$

where B_d is the same parameter as in eq 1. According to eq 8, E_D/RT for CO_2 are plotted against $T(v_{h,Ps}I_{3,a})^{-2}d(v_{h,Ps}I_{3,a})/dT$ in Figure 4.

There is a rough correlation between them. However, the B_d' value, 0.19 nm^3 , evaluated from the correlation line is much different from the value (0.14 nm^3) evaluated from the correlation between $\log(D_a/T)$ and $(v_{h,Ps}I_{3,a})^{-1}$.

In a previous paper, we found that $\log D$ for CO_2 and CH_4 in a series of polyimides at 308 K was correlated more clearly to $v_{h,Ps}$ than to $v_{h,Ps}I_{3,a}$.¹³ Recently, we have proposed a method to evaluate $C_{h,Ps}$ and $V_{F,Ps}$ from τ_3 and V_F on some assumptions, and predicted that there is a correlation between $V_{F,Ps}$ and $v_{h,Ps}$ but not between $C_{h,Ps}$ and I_3 for the rubbery polymers.⁹ Then, we next examine how clearly $\log(D_a/T)$ is correlated to $v_{h,Ps}^{-1}$. As shown in Figure 5, there is a correlation between $\log(D_a/T)$ and $v_{h,Ps}^{-1}$, although the data for larger $v_{h,Ps}^{-1}$ are rather scattered. The data point for 6FDA-DAH PI is almost on the correlation line. As shown in Figure 6, there is a rough linear correlation between E_D/RT and $Tv_{h,Ps}^{-2}dv_{h,Ps}/dT$ with the slope equal to the B_d'' ($=B_d v_{h,Ps}/f$) value, 0.90 nm^3 evaluated from the correlation between $\log(D_a/T)$ and $v_{h,Ps}^{-1}$.

These results reveal that diffusion of gaseous penetrants in the rubbery polymers at temperatures not much above T_g is well described

by the free volume model using $v_{h,Ps}$ rather than $v_{h,Ps}I_{3,a}$ for f in eq 1 and 8. This seems to be because $v_{h,Ps}$ is correlated to $V_{F,Ps}$ and, as a result, to $V_{F,dif}$.⁹

Correlation of D with $V_{F,dif}$

Now, we apply the method used for evaluation of $V_{F,Ps}$ to evaluate $V_{F,dif}$. Free volume holes of rubbery polymers have the size distribution of exponential type (eq 7). The volume fraction of total free volume holes is reasonably assumed to be equal to V_F calculated by eq 4.

$$V_F = \int_0^{\infty} C_{h,t} f(v_h) v_h dv_h = \langle v_h \rangle C_{h,t} \quad (9)$$

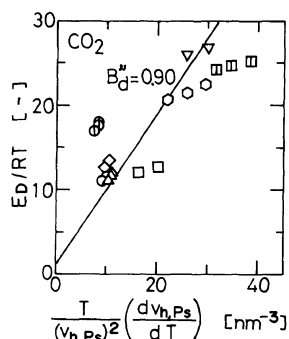


Figure 6. Plots of E_D/RT versus $T v_{h,Ps}^{-2} dv_{h,Ps}/dT$ for rubbery polymers. The symbols are as in Figure 1.

where $C_{h,t}$ is the concentration of total free volume holes. It is not clear whether o -Ps is trapped in all the free volume holes larger than the critical size $a=0.033 \text{ nm}^3$ with equal probability. It is probable that o -Ps is trapped in a larger free volume holes with a larger probability. Therefore, taking the function $g(v_h)$ which describes the ease of trapping o -Ps into consideration, average size, volume fraction, and concentration of free volume holes probed by o -Ps, $v_{h,Ps}$, $V_{F,Ps}$, and $C_{h,Ps}$, respectively, are described by eq 10, 11, and 12.

$$v_{h,Ps} = \int_a^{\infty} v_h f(v_h) g(v_h) dv_h / \int_a^{\infty} f(v_h) g(v_h) dv_h \quad (10)$$

$$V_{F,Ps} = C_{h,t} \int_a^{\infty} v_h f(v_h) g(v_h) dv_h = v_{h,Ps} C_{h,Ps} \quad (11)$$

$$C_{h,Ps} = C_{h,t} \int_a^{\infty} f(v_h) g(v_h) dv_h \quad (12)$$

As $g(v_h)$, we tentatively use the following function.

$$g(v_h) = 1 - \exp[-b(v_h - a)] \quad (13)$$

For an assumed value of b in eq 13, $\langle v_h \rangle$ of a rubbery polymer at temperature T is determined from the observed value of $v_{h,Ps}$ by

Table III. Free volume properties of the polymers at T_g evaluated from the PA data by the model^a

Polymer	τ_3	I_3	$v_{h,Ps}$	$\langle v_h \rangle$	$C_{h,t}$	V_F	$V_{F,Ps}$	$V_{F,dif}$
	ns	%	nm^3	nm^3	nm^{-3}	—	—	—
1,2-PB	1.96	33.0	0.093	0.038	4.61	0.175	0.076	0.144
1,2-PB ^b	2.46	36.7	0.143	0.079	2.51	0.198	0.144	0.188
PE ^c	2.62	25.7	0.159	0.093	2.10	0.196	0.152	0.188
PMA	1.72	23.5	0.072	0.023	6.58	0.151	0.034	0.097
P4MP-C	2.55	20.0	0.152	0.087	2.39	0.207	0.157	0.198
PBMA	2.42	29.4	0.138	0.075	2.24	0.167	0.118	0.158
PVAC	1.95	23.4	0.092	0.037	4.73	0.177	0.076	0.145
PET	1.86	20.4	0.084	0.032	5.13	0.162	0.058	0.125
PS	2.34	32.2	0.130	0.068	2.86	0.194	0.131	0.181
6FDA-DAH	1.96	6.4	0.093	0.038	4.06	0.154	0.067	0.127

^a $\langle v_h \rangle$, $C_{h,t}$, $V_{F,Ps}$, and $V_{F,dif}$ were calculated for $b=20$ in $g(v_h)$.

^b At $(T_g + 44)$ K.

^c At $(T_g + 52)$ K.

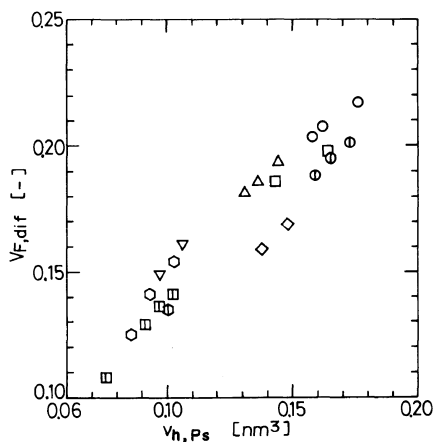


Figure 7. Plots of $V_{F,dif}$ calculated for $b=20$ in $g(v_h)$ versus $v_{h,Ps}$ for rubbery polymers. The symbols are as in Figure 1.

eq 10, then $C_{h,t}$ is determined from the value of V_F by eq 9, and finally $C_{h,Ps}$ and $V_{F,Ps}$ are calculated by eq 11 and 12. The results calculated for the assumed values of b from 20 to infinite are not much different each other. In a first approximation, we presume that all the free volume holes larger than $v_h = 0.029 \text{ nm}^3$ can equally contribute to the diffusion of CO_2 and CH_4 , and then $V_{F,dif}$ is given by

$$V_{F,dif} = C_{h,t} \int_{0.029}^{\infty} v_h f(v_h) dv_h \quad (14)$$

Free volume properties of the polymers at T_g evaluated thus from the PA data are listed in Table III. Among the polymers investigated here, $\langle v_h \rangle$ varies from 0.023 nm^3 (0.35 nm in diameter) for PMA to 0.087 nm^3 (0.55 nm) for P4MP-C. For P4MP-C, the $\langle v_h \rangle$ value is much larger than the effective size of the penetrants, 0.029 nm^3 (0.38 nm in diameter) and the $V_{F,dif}$ value is only 4% smaller than the V_F value. On the other hand, for PMA, the $\langle v_h \rangle$ value is a little smaller than the effective size of the penetrants and the $V_{F,dif}$ value is only 64% as large as V_F . Figure 7 shows plots of $V_{F,dif}$ versus $v_{h,Ps}$ for the rubbery polymers. There is a correlation

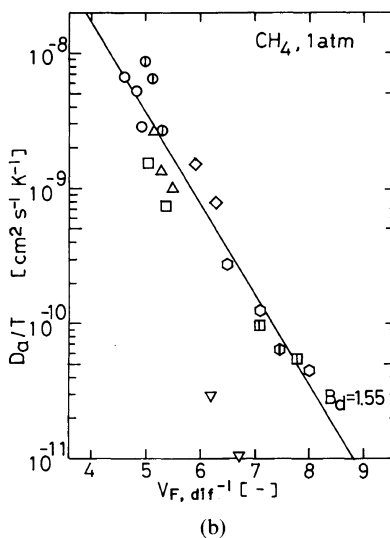
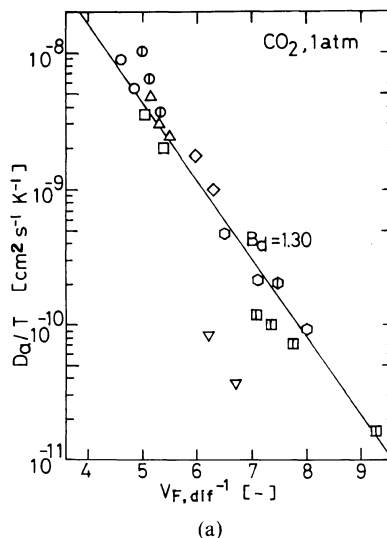


Figure 8. Plots of $\log(D_a/T)$ versus $V_{F,dif}^{-1}$ for rubbery polymers. The symbols are as in Figure 1.

between $V_{F,dif}$ and $v_{h,Ps}$; polymers with larger $v_{h,Ps}$ or $\langle v_h \rangle$ have larger $V_{F,dif}$.

As shown in Figure 8, there are clear correlations between $\log(D_a/T)$ and $V_{F,dif}$ for CO_2 and CH_4 in all the rubbery polymers investigated except for PVAC. As shown in Figure 9, there is a rough correlation between E_D/RT and $TV_{F,dif}^{-2}(dV_{F,dif}/dT)$ with the slope equal to the B_d value (1.3) for CO_2

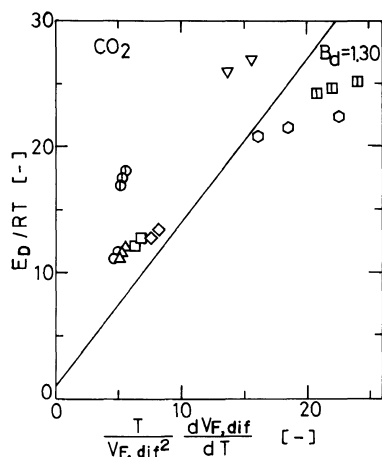


Figure 9. Plots of E_d/RT versus $TV_{F,dif}^{-2}dV_{F,dif}/dT$ for rubbery polymers. The symbols are as in Figure 1.

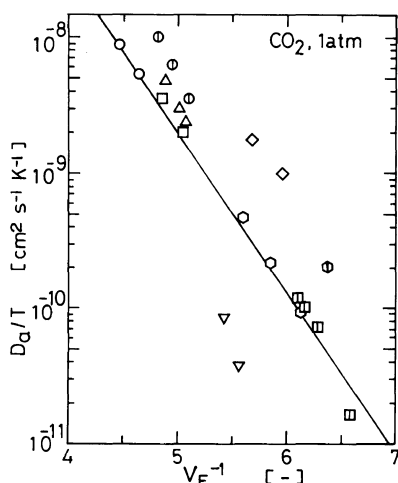


Figure 10. Plots of $\log(D_a/T)$ versus V_F^{-1} for rubbery polymers. The symbols are as in Figure 1.

evaluated from the correlation line in Figure 8. As shown in Figure 10, $\log(D_a/T)$ is correlated to V_F^{-1} with somewhat large scattering. It is noteworthy that D is correlated better with $V_{F,dif}$ than with V_F ; the correlation is improved by taking the size distribution of free volume holes into account. In the present model, for the polymers having relatively large V_F , the $V_{F,dif}$ values are only slightly different from the V_F values, because the $\langle v_h \rangle$ is much larger than the effective size of the

penetrants. On the other hand, for the polymers having relatively small V_F , the $V_{F,dif}$ values are fairly different from the V_F values, depending on the magnitude of $\langle v_h \rangle$. The $\langle v_h \rangle$ values of PBMA and 6FDA-DAH PI are larger than those for PET and PMA, respectively, and as a result the data points for the formers are upward away from the correlation line between $\log(D_a/T)$ and V_F^{-1} . This is corrected in the plots of $\log(D_a/T)$ versus $V_{F,dif}^{-1}$, resulting in the better correlation.

The validity of the free volume properties evaluated by the present model crucially depends on the validity of the estimated value of the fractional volume of whole free volume holes. The best way to estimate this is believed to be the method developed by van Krevelen¹⁵ and used in present study. The limitation of the present model lies in this point. The data point of PVAC are far away from both the correlation lines of $\log(D_a/T)$ with $V_{F,dif}^{-1}$ and V_F^{-1} , of which the reason may lie in the validity of the estimated value of V_F of PVAC.

Acknowledgements. This work was supported by a Grand-in-Aid for Scientific Research (No. 03650729) from the Ministry of Education, Science, and Culture of Japan.

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